

# Resonant Inelastic X-Ray Scattering of Insulating Cuprates at the Oxygen 1s-Resonance

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## INTRODUCTION

The insulating cuprates comprise an interesting subgroup of the 3d transition metal compound family because of their intriguing low-temperature behavior. It is well known that many insulating cuprate compounds are antiferromagnetic at room temperature and that they upon doping, for instance with Group IIb elements, can exhibit a superconductive phase at low temperatures. Orthorhombic  $\text{CuGeO}_3$  is unusual as a cuprate in that it possesses a phase transition to a spin-Peierls state below  $T_{\text{sp}} = 14$  K. In order to understand the underlying mechanisms for these kinds of phase transitions it is essential to obtain better understanding of the electronic structure of these materials also at room temperature. One may consider the Cu-O octahedra of these compounds as basic building blocks that are coupled in various geometries, the details of which most likely give rise to the peculiarities of their macroscopic behavior. Core level spectroscopies reflect local excitations and lend themselves for studying the electronic structure of these Cu-O networks in detail.

## EXPERIMENTAL

The investigated samples were large single crystals of  $\text{CuGeO}_3$ ,  $\text{CuO}$ ,  $\text{LaCuO}_4$ , and  $\text{SrCuO}_2$ . The experiments were performed at the undulator beam line 7.0.1 with a spherical-grating monochromator at the Advanced Light Source (ALS), Lawrence Berkeley Laboratory. The soft x-ray absorption spectra (SXAS) were measured by recording the total electron yield (TEY) and the fluorescence yield (FY) while scanning the photon energy of the incident monochromatized synchrotron radiation. The monochromator energy band pass used for all SXAS spectra and for the resonantly excited SXES spectra was approximately 0.15 eV. TEY absorption spectra were recorded by measuring sample current and FY absorption spectra were measured with a channel electron multiplier. The SXAS spectra were normalized to the photocurrent from a clean gold mesh introduced into the synchrotron radiation beam in order to correct for intensity variations of the incident x-ray beam. The soft x-ray emission spectra (SXES) were recorded with a high-resolution Rowland-mount grazing-incidence grating spectrometer with a two-dimensional detector at a resolution of about 0.15 eV. All experiments were performed with the samples at room temperature.

## RESULTS

Figure 1 shows RIXS at O 1s-resonance of  $\text{CuGeO}_3$ ,  $\text{CuO}$ ,  $\text{LaCuO}_4$ , and  $\text{SrCuO}_2$ . Usually, O K-absorption and emission reflect the local density of unoccupied respectively occupied O 2p-states rather well. However, when exciting at the pre-peak structure of the O K-absorption edge it has been recently shown that RIXS features appear between the main fluorescence band and the elastic peak.

For  $\text{CuGeO}_3$  the RIXS part of the resonant O K-emission has been interpreted [1] as a signature for a dd-excitation which previously only has been observed for excitation at Cu p-resonances. The excitation energy for dd-excitations of  $\text{CuGeO}_3$  is being debated in current literature, but our experimental value ( $1.64 \pm 0.1 \text{ eV}$ ) agrees well with the most recent results obtained by optical absorption spectroscopy [2]. We have studied O 1s-RIXS of  $\text{CuGeO}_3$  with different detection angles and show the result as the upper two spectra in Fig. 1. Horizontal detection corresponds to the situation when the scattered photons propagate parallel with the polarization vector of the incoming photons. Vertical detection corresponds to detection where the two directions make a right angle. There is no change in the energy position of the dd-excitation whereas the main fluorescence band (expectedly) changes shape due to change in weight of states from different symmetry. Moreover, the elastic peak is more prominent in the RIXS from the vertical detection symmetry due to geometrical enhancement.

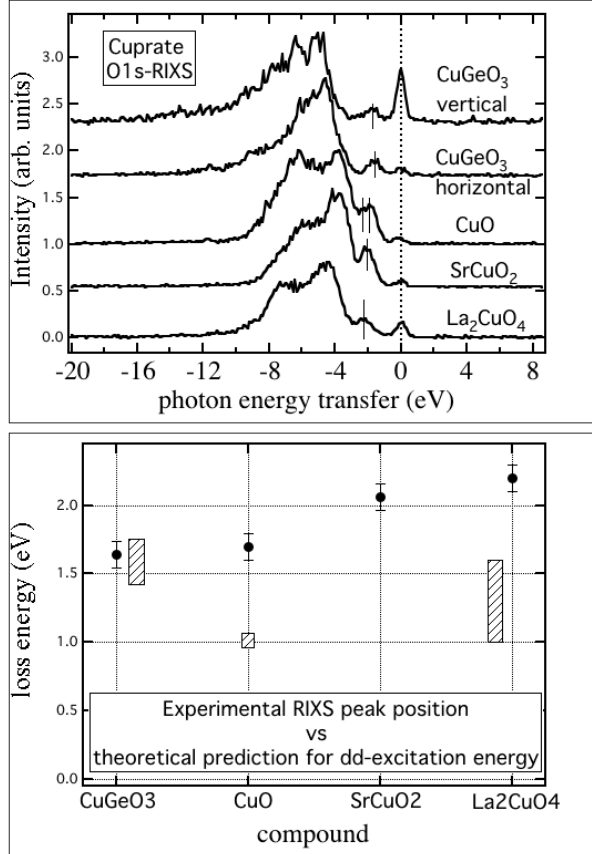


Figure 1. Top panel: O K-RIXS for various compounds excited at prepeak on an energy transfer scale (top 2 spectra have been detected in vertical detector position and horizontal detector position respectively). Bottom panel: energy locations of the first energy loss structure. Circles show the data taken in this work (top panel) and the hatched rectangles show theoretical predictions from literature.

## DISCUSSION

We observe extraordinarily high excitation energies of the O 1s RIXS features of  $\text{CuO}$ ,  $\text{LaCuO}_4$ , and  $\text{SrCuO}_2$  compared to expected dd-excitations energies. Theoretical work by Okada and Kotani [4] show structures at similar energies and they interpret these as a kind of Zhang-Rice singlet (ZRS). ZRS have been related to the first ionization state of transition metal oxides and have been sought in valence band photoemission spectra of such compounds. However, it is

For  $\text{CuO}$ ,  $\text{LaCuO}_4$ , and  $\text{SrCuO}_2$ , however, we measure significantly higher loss values for the RIXS features. A comparison with theoretical predictions, as far as available [3], shows (Fig. 1, bottom panel) that dd-excitations are expected at much lower energies. Instead, another mechanism has been invoked to explain the relatively large energy values of this local excitation, namely formation of a Zhang-Rice singlet. A recent model calculation using the Anderson impurity approach shows [4] that both types of excitations are expected to be present in O 1s-RIXS, but their relative intensity and energy separation depend on the value of the model parameter that describes the charge transfer energy between the Cu 3d and O 2p states. Thus measuring O 1s-RIXS can give valuable input for such model calculations, restricting the range of parameter values.

puzzling that the ZRS so far has only been identified in one clearcut case, namely in the photoemission spectra of CuO. These states should in principle show up in resonant SXES when exciting with a photon energies above the ionization threshold. The ZRS state presents a combination of several two-hole states, but mainly one with one electron ionized from the O 2p-band. Thus one should expect a signature of this excitation just above the main fluorescence band that follows ionization by core hole excitation. In the same energy region, i.e above the main fluorescence band, lie also the charge neutral dd-excitations.

At resonance excitation, signatures from localized final states should dominate the RIXS spectra, including charge transfer (CT) and dd-excitations. CT excitations in the sense used here involves the transfer of a Cu 3d-electron to the O 2p-band and they are thus charge neutral. Usually such a rearrangement is of much higher energy cost than the other two possibilities discussed. CT have been measured for CuGeO<sub>3</sub> by Cu 2p-RIXS showing up as a band between 3.5-8 eV energy loss. Observation of dd-excitations in O1s-RIXS would present a correlation effect between the Cu 3d-states and the O 2p-states since the direct overlap of the O1s core wavefunction and Cu 3d-states should be negligible. However, dd-excitations have been calculated [3] and measured [2] to have significantly lower energies than the RIXS features under discussion. On the other hand, recent RIXS experiments at the Cu 3p-resonances by our group reveal that at least some dd-excitations of these compounds are indeed found at higher energies than previously assumed. This strengthens the conclusion that also the O1s RIXS peaks that we observe are related to the dd-excitation mediated by a kind of interatomic correlation effect. More experiments using higher resolution and polarization dependence are desirable and underway. It is clear however, that oxygen 1s-RIXS is a valuable tool for studying local excitations of correlated oxides such as cuprates.

## SUMMARY

O1s RIXS has been performed on several insulating cuprates. Excitation at the O1s-absorption pre-peak shows Raman-like energy loss features at similar energies as for Cu M-edge RIXS. We believe this to be evidence for a inter-atomic correlation effect between O 2p- and Cu 3d-states.

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